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Enhancing the mechanical properties of single-crystal CVD diamond

Qi Liang, Chih-shiue Yan, Yufei Meng, Joseph Lai, Szczesny Krasnicki, Ho-kwang Mao and Russell J Hemley

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, USA

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Abstract

Approaches for enhancing the strength and toughness of single-crystal diamond produced by chemical vapor deposition (CVD) at high growth rates are described. CVD processes used to grow single-crystal diamond in high density plasmas were modified to incorporate boron and nitrogen. Semi-quantitative studies of mechanical properties were carried out using Vickers indentation techniques. The introduction of boron in single-crystal CVD diamond can significantly enhance the fracture toughness of this material without sacrificing its high hardness (~ 78 GPa). Growth conditions were varied to investigate its effect on boron incorporation and optical properties by means of photoluminescence, infrared, and ultraviolet–visible absorption spectroscopy. Boron can be readily incorporated into single-crystal diamond by the methods used, but with nitrogen addition, the incorporation of boron was hindered. The spectroscopic measurements indicate that nitrogen and boron coexist in the diamond structure, which helps explain the origin of the enhanced fracture toughness of this material. Further, low pressure/high temperature annealing can enhance the intrinsic hardness of single-crystal CVD diamond by a factor of two without appreciable loss in fracture toughness. This doping and post-growth treatment of diamond may lead to new technological applications that require enhanced mechanical properties of diamond.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With its intrinsic hardness of ~ 100 GPa, natural single-crystal diamond continues to play a singularly important role in a variety of scientific and industrial applications [1, 2]. However, diamond is also known as a brittle material with a fracture toughness (K_{IC}) between 7.0 and 8.4 MPa m^{1/2} for type Ia diamond and between 4.2 and 5.6 MPa m^{1/2} for type IIa diamond [3, 4], and this limits performance for many applications. Polycrystalline diamond (PCD), is perhaps the most commonly used tough diamond [5]. However, the hardness of PCD is adversely affected by the soft metal binder phase and its intergrain sp² carbon interactions. Diamond post-treatments have also been reported to enhance its toughness. High temperature annealing at temperatures greater than 1100 °C has been used to remove the intrinsic and the diamond/substrate thermal mismatch stresses in diamond

films grown by chemical vapor deposition (CVD) [6]. Anthony *et al* [7] strengthened diamond by applying a thin shell of impurities containing diamond to create a compressive stress on the diamond outer surface. The added strength is lost once the shell is breached.

It has been proposed that the strength of CVD diamond can be improved by doping and managing the stress distribution with dopants such as nitrogen, boron or hydrogen [8]. The intrinsically strongest diamond crystals proposed only exhibit (111) and/or (100) growth facets and sectors. Recent improvements in growing single-crystal CVD (SC-CVD) diamond by MPCVD have enabled fabrication of large (>3 carats), high quality diamond at very high growth rates [9–11]. A gas chemistry of H₂/CH₄/N₂ for the diamond growth was used in the MPCVD process, and the (100) growth surface was significantly enhanced. Ultrahigh hardness (>150 GPa) and improved toughness have been reported for

such crystals [12]. It has been reported that boron can be preferentially incorporated in the (111) sector in both gem and CVD diamond [13]. Substitutional boron expands the diamond lattice and its solubility in diamond can be as much as 0.9% [7]; an improvement in crystal optical quality has also been reported [13, 14]. For decades, researchers have focused on the electronic properties and applications of boron doped diamond [13–15]. There is less information on the mechanical properties of boron doped diamond.

The determination of fracture toughness (K_{IC}) for material with mechanical properties close to diamond has been challenging. The most common method is indentation, a technique first used by Field *et al* [16] with blunt indenters and further explored by Novikov *et al* [3, 4] with Vickers indenters. Vickers micro-hardness testing techniques have been widely used to evaluate the hardness and fracture toughness of diamond [3, 4, 12, 17]. Using these approaches, we have demonstrated that high growth rate SC-CVD diamond has extremely high hardness [12]. In this study, an identical methodology was employed to study the hardness/toughness evolution after selective doping. We report a dramatic enhancement of intrinsic fracture toughness of SC-CVD diamond by selective doping with nitrogen and boron. We also report a significant enhancement of mechanical properties after low pressure/high temperature post-growth annealing.

2. Experimental methods

Boron-containing single-crystal diamond was synthesized by high density MPCVD at 5–20% CH_4/H_2 , 0–0.2% N_2/CH_4 , at 150–220 Torr and at temperatures ranging from 1100 to 1300 °C, as measured by a two-color IR pyrometer. Inert hexagonal boron nitride powder (h-BN) was selected as the dopant and introduced into the CVD system by placing in between the molybdenum holders used to hold the diamond substrate. The decomposition of h-BN in the plasma system supplies a sufficient amount of boron for the doping process. And the amount of h-BN involved in the reaction can be determined by measuring the weight loss of the h-BN powder after the diamond growth. Commercial HPHT synthetic Ib diamond plates (5 mm × 5 mm × 0.3 mm) were used as substrates. The growth surfaces were within 3° of the {100} top plane. A growth rate of 20–100 $\mu\text{m h}^{-1}$ was recorded, which is a 10–100 times improvement in the growth rate as compared with other boron doped single-crystal diamond growth. After the growth, CVD layers were separated from the substrates by a Bettonville–Combi laser cutting system with a Q-switched Nd:YAG laser operated at a wavelength of 0.8 μm , followed by fine polishing to remove any residual carbon. Undoped SC-CVD crystals free of visible defects in the size range of 0.2–6 mm were selected for low pressure/high temperature (LPHT) annealing. The 6 kW 2.45 GHz MPCVD reactor used for growth/annealing was used. The annealing was carried out with a measured diamond surface temperature 1600–2200 °C at gas pressures between 150 and 300 Torr. A Vickers micro-hardness tester was used to evaluate the fracture toughness of the boron doped single-crystal CVD diamond produced. To validate the indentation results, all indenters were

inspected under a microscope and tested on a polished metal surface before and after each successful diamond indentation. Photoluminescence spectra were obtained at room temperature using an ion-argon laser operating at 514.5 nm. The infrared spectra were measured using synchrotron radiation at the National Synchrotron Light Source (beamline U2A), with a Bruker IRScope II spectrometer with 1 cm^{-1} resolution. UV-visible spectra were obtained in a home-built spectrometer with a focal beam size of $\sim 10 \mu\text{m}$.

3. Results and discussion

Quantifying mechanical properties such as fracture toughness for materials such as diamond is challenging. Although Vickers micro-hardness testing techniques have been used to evaluate both the hardness and fracture toughness of diamond, however, ambiguity arises when Vickers indenters are used against material with a hardness comparable or exceeding that of the indenter material (i.e., single-crystal diamond). Hardness values higher than 120 GPa, in which deformation of the indenting tip occurs, are unrealistic [18]. However, the consistency of the values obtained with other types of diamonds whose mechanical properties have been determined by a variety of approaches demonstrates that this method is capable of providing semi-quantitative results. The technique is also useful for comparing mechanical properties of superhard materials generally [12]. In the present study, an identical methodology was employed to study the hardness/toughness of boron/nitrogen co-doped and LPHT treated SC-CVD diamond.

Hardness–fracture toughness data are plotted in figure 1 for natural Ia, IIa, synthetic Ib, SC-CVD, boron/nitrogen co-doped SC-CVD diamonds, HPHT and LPHT annealed SC-CVD diamonds. To prevent plastic deformation, low loads between 1 and 3 kg were used. All tests were done in the same Vickers indenter tester at different times; natural Ia, IIa, synthetic Ib and selected measurements from our previous work on the SC-CVD diamond are shown [12]. Our measurements are consistent with published values for natural IIa diamond (4.2–5.6 $\text{MPa m}^{1/2}$) [4], which presumably has a higher hardness and thus a higher probability of damaging the diamond tips. Nevertheless, the results may be considered comparable in terms of their hardness/toughness values. Without boron doping, SC-CVD diamond grown by $\text{H}_2/\text{CH}_4/\text{N}_2$ chemistry has a fracture toughness of 15.2(± 4.8) $\text{MPa m}^{1/2}$, compared with 8(± 4) $\text{MPa m}^{1/2}$ for natural Ia, IIa, and colorless CVD single-crystal diamond grown without the addition of N_2 as a feed gas, and 10(± 2) $\text{MPa m}^{1/2}$ for Ib synthetic yellow diamond. The fracture toughness of boron/nitrogen co-doped SC-CVD diamond is between 22 and 34 $\text{MPa m}^{1/2}$. It is clear that boron doping of SC-CVD diamond significantly improves the fracture toughness by at least a factor of two, without compromising the hardness (78(± 12) GPa).

The measurements further reveal that the LPHT annealed SC-CVD exhibits ultrahard characteristics (measured hardness of at least ~ 125 GPa) without an appreciable reduction in toughness ($K_{IC} = 12\text{--}16 \text{ MPa m}^{1/2}$). This contrasts with

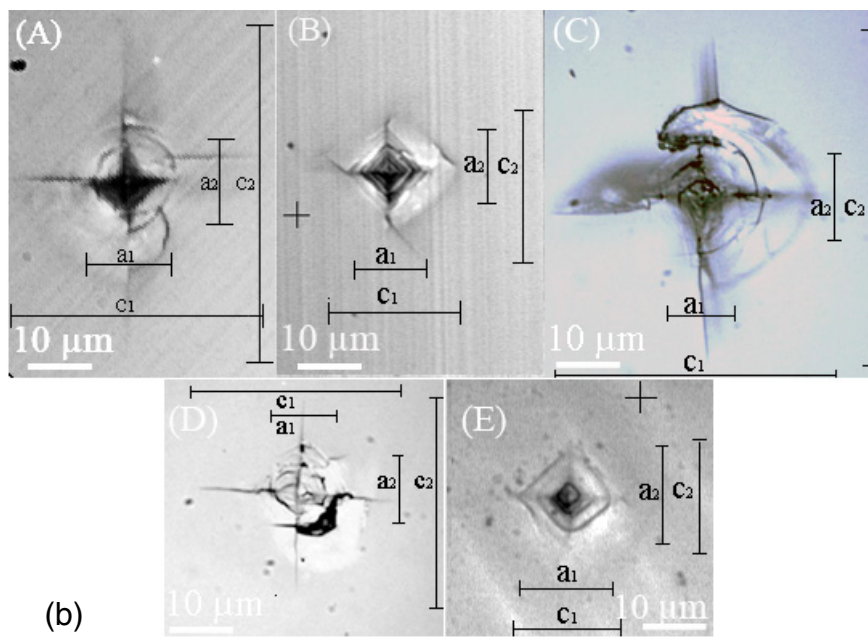
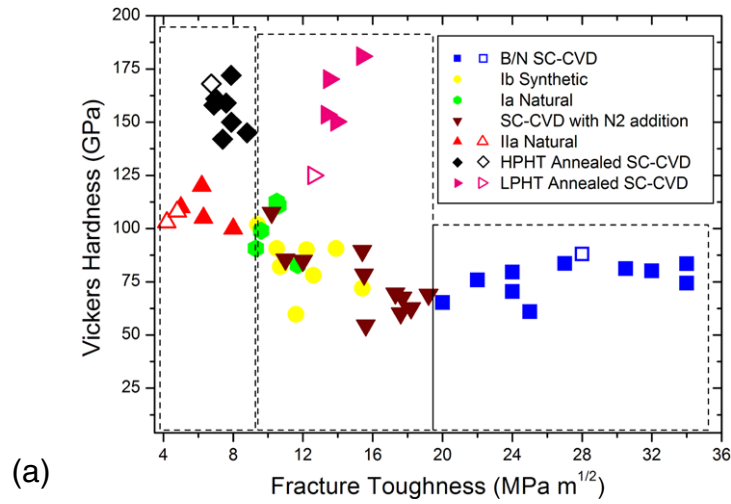


Figure 1. (a) Vickers hardness and fracture toughness on [100] faces of various diamonds in the {100} direction. Three zones are defined: on the left are the reported and measured values for natural type Ia and IIa diamond; the center zone includes type Ib and CVD diamond; the right zone includes boron doped CVD diamond. Micrographs in figure 1(b) correspond to the hollow data points. Hollow data points refer to the micrographs in figure 2. (b) Selected images of indentation patterns on diamonds.

Type of diamond	Treatment	Nominal Vickers hardness (GPa)*	Nominal fracture toughness (MPa m ^{1/2})*	
A	Natural type IIa	None	100	4.2
B	SC-CVD	LPHT	125	13
C	Natural type IIa	None	110	4.8
D	SC-CVD	HPHT	170	6.5
E	B/N-SC-CVD	None	88	28

* denotes ±5% random error; systematic error is difficult to quantify because different techniques will give different results for hardness and toughness (e.g. [30]). Hence we consider these measurements to be semi-quantitative. On the other hand, they do provide a robust comparative indication of variations in mechanical properties of these diamond materials. Vickers hardness and fracture toughness were estimated based on the indentation size $2a$, where $a = (a_1 + a_2)/2$ and the length of radial cracks measured from the indent center $c = (c_1 + c_2)/4$ [12, 17].

the results obtained previously for SC-CVD subjected to high pressure/high temperature (HPHT) annealing [12]. Recently, annealing studies of these diamonds under low pressure/high temperature (LPHT) conditions (>1600 °C, <300 Torr; i.e., outside the diamond stable field) revealed major changes in optical properties, including decreases in visible absorption [19].

Although it may be argued that *quantitative* measurements on materials having fracture toughnesses higher than 30 MPa m^{1/2} exceed the limit of Vickers techniques, it is important to note that the behavior of the diamond material studied here is *qualitatively* different. Specifically, the lack of a visible trace of cracking along the indentation craters

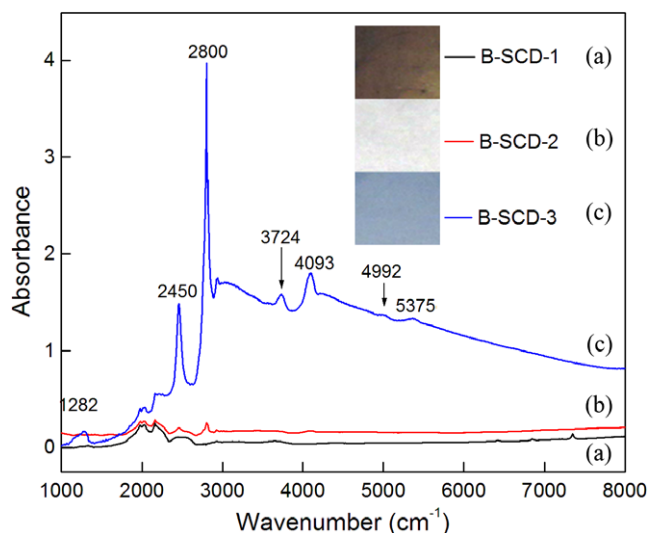


Figure 2. IR absorption spectra for representative materials B-SCD-1, B-SCD-2, and B-SCD-3 (300 K). All materials have identical thickness (~ 0.3 mm). The inset shows surface images of the three materials in this measurement, the color of these materials are brown, transparent, and blue, respectively.

is remarkable (figure 1). All indentation marks on the boron/nitrogen co-doped SC-CVD diamond (e.g., B-SCD) exhibit square crack patterns along the softer $\{110\}$ and $\{111\}$ directions, but the material is free of crack lines along $\{100\}$. Unlike indentation craters on natural or type Ib diamonds, which typically contain cross-like cracks along all of the above directions, the fracture pattern on B-SCD is more predictable and can be engineered to further improve fracture resistance in mechanical and abrasive applications. We therefore define this class of diamonds as ultratough.

Three representative materials with distinct optical appearances were selected for further characterization (i.e., B-SCD-1, -2, and -3). With the exception of the different nitrogen flow rate (0.1, 0.06, 0.03 sccm, respectively), the growth parameters were identical, as was the thickness of these materials (~ 0.3 mm). Dramatic color differences can be attributed to the boron and nitrogen concentration in the diamond structure (figure 2). The toughness data for these materials show some scatter (figure 1(a)), but we find that in general, we find that materials with high B and N content have significantly higher toughness. The IR absorption spectra of these materials are plotted in figure 2. Spectra for blue (B-SCD-3) and transparent (B-SCD-2) materials clearly show (1) the boron induced one phonon absorption around 1282 cm^{-1} ; (2) electronic excitations at 2457 and 2800 cm^{-1} ; (3) one phonon assisted transition at 3724 , 4093 cm^{-1} ; and (4) the two phonon assisted transitions at 4992 and 5375 cm^{-1} . For material B-SCD-1, similar to nitrogen doped CVD single-crystal diamond, in the near-IR region, the main absorption lines at 7357 , 7220 , 6856 , 6429 , and 5567 cm^{-1} accompany a continuously increasing absorption from 5000 to 8000 cm^{-1} . In the CH stretching vibration region (2700 – 3100 cm^{-1}), a broad absorption band centered around 2925 cm^{-1} is observed for all three representative materials. For B-SCD-2 and B-

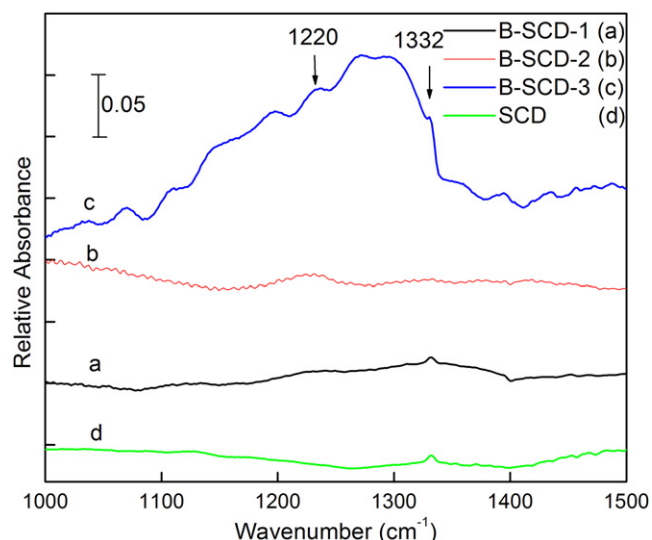


Figure 3. Detail of the IR absorption spectra in the 1000 – 1500 cm^{-1} region for representative materials B-SCD-1, B-SCD-2, B-SCD-3, and SCD (300 K). Material SCD was grown under the same conditions as B-SCD-1 but is free of boron incorporation.

SCD-3, a small shoulder around 2759 cm^{-1} appears near the 2800 cm^{-1} band.

The determination of uncompensated boron concentration by IR spectroscopy has been thoroughly investigated for both natural [20] and CVD [21] diamond. Gheeraert *et al* [21] have shown that for CVD boron doped homepitaxial CVD diamond films, the uncompensated boron concentration (B) can be determined by the integrated intensity of the 2800 cm^{-1} peak through the relation $(B)\text{ (cm}^{-3}) = 1.1 \times 10^{15} I_{(2800\text{ cm}^{-1})}\text{ (cm}^{-2})$. Based on this model, uncompensated boron concentrations for B-SCD-2 and B-SCD-3 are 0.20 and 4.02 ppm, respectively. No uncompensated boron could be found in B-SCD-1. Three factors are considered to account for the dramatic increase in incorporated boron with the slight increase in nitrogen flow rates: (1) the interaction between nitrogen and boron in the plasma [22]; (2) the competing growth between the nitrogen atom preferred (100) growth sector and the boron atom preferred (111) growth sector; (3) the amount of boron that is compensated by the nitrogen within the diamond crystals (which cannot be identified by IR).

A sharp decrease in boron concentration was observed by Liang *et al* [23] in the synthesis of boron doped nanocrystalline diamond films using $\text{H}_2/\text{CH}_4/\text{N}_2/\text{B}_2\text{H}_6$ chemistry by adjusting nitrogen flow rates. A similar effect was observed by Sonoda *et al* [24] while adjusting the nitrogen addition on the order of 100 ppm in the reaction gas of a CVD system. For B-SCD-1 an important consideration is how much boron exists in the diamond structure and how it interacts with adjacent carbon and nitrogen atoms; IR absorption at lower wavenumbers (1000 – 1500 cm^{-1}) differs from single-crystal diamond grown under the same conditions without boron in the reaction chemistry (figure 3). However, there is currently little information on the interaction mechanisms between boron and nitrogen in diamond crystals, and a satisfactory explanation cannot yet be provided. It is clear from figure 2 that the

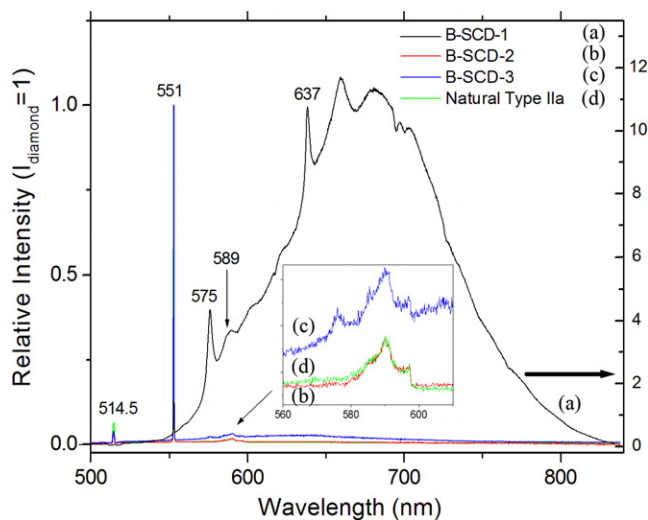


Figure 4. Photoluminescence (PL/Raman) spectra taken with the 514.5 nm laser line at room temperature on a natural IIa diamond, B-SCD-1, B-SCD-2, and B-SCD-3. The intensity scales were normalized to the diamond first-order Raman peak. The inset shows spectral details in the 570–610 nm range for spectra taken from IIa, B-SCD-2, and B-SCD-3.

concentration of uncompensated boron also determines the color of the crystals; the blue color was vivid for diamond with a high concentration of uncompensated boron, with a low concentration of uncompensated boron, the crystal is clear. Nitrogen impurities dominate the diamond crystal, in part giving rise to the light brown color.

Photoluminescence (PL) spectra of these three representative materials are presented in figure 4. The major peaks are: diamond peak at 551 nm, NV^0 center at 575 nm and NV^- center at 673 nm. On the spectrum of B-SCD-1, there is also a broad, previously unreported center occurring around 589 nm. Compared with CVD diamond grown under the same conditions but without boron incorporated, the broad PL background decreased significantly, and was accompanied by a tenfold increase in $I_{D@551\text{ nm}}/I_{NV@575\text{ nm}}$ (ratio of integrated intensity of the diamond Raman peak and NV^0 center). The improvement in crystal quality is further seen in the spectra of B-SCD-2 and B-SCD-3; the broad PL background is nearly flat, with the second-order Raman feature arising between 580 and 600 nm. The optical properties of these materials and natural IIa diamond were further investigated by UV–visible absorption spectroscopy (figure 5). B-SCD-1 exhibits typical features of brown CVD diamond: broad bands at 270 nm (substitutional nitrogen), 370 and 550 nm (nitrogen vacancy center). These bands are not found in the spectra of either B-SCD-2 or B-SCD-3. The lineshape of B-SCD-2 is very similar to that of natural IIa diamond, and there is an obvious blue hue in B-SCD-3.

Incorporation of nitrogen in the growth chemistry significantly enhances the formation of the (100) growth facets, as nitrogen atoms preferably incorporate into the (100) growth surface [10, 25]. However, boron species greatly enhance the formation of octahedral growth facets and preferably incorporate into the (111) growth surface [20]. Therefore the enlargement of the boron doped CVD diamond layer

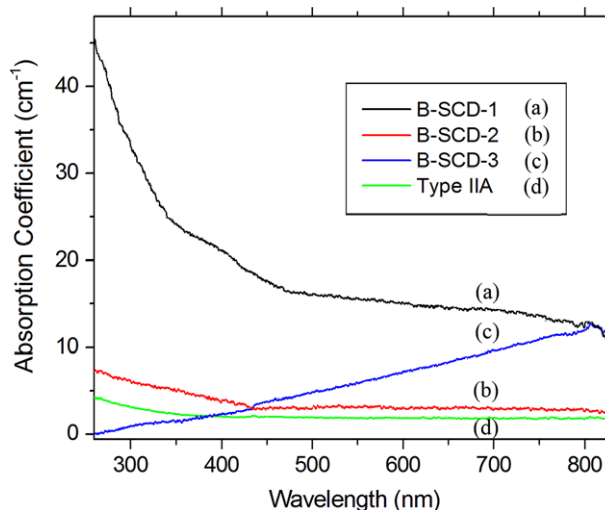


Figure 5. UV–visible spectra of four diamond materials (natural IIa, B-SCD-1, B-SCD-2, and B-SCD-3) recorded at room temperature.

is not applicable due to the discontinuity in the octahedral structure [26]. Diamond substrates in this study were oriented to within 3° of the (100) plane (the uncertainty in the laser sawing technique). The co-doping mechanism can be illustrated by the step-flow growth process first discussed by Tsuno *et al* [27]. Nitrogen atoms would enhance the formation of the micro-terraces, while boron atoms can be doped between individual steps. A continuous step-flow growth surface is thereby formed for further CVD layer enlargement.

Unlike diamond treated for surface toughening by ion-implantation [28] or surface thermal diffusion [29], all CVD diamond crystals in this study were extensively polished prior to indentation. The results therefore demonstrate that the toughness enhancement is a bulk property. The IR and PL spectra indicate that boron and nitrogen (NV^0 center at 575 nm) atoms do coexist in the diamond structure (e.g., spectrum of B-SCD-3). Measurements to date lead us to propose that the interaction among nitrogen, boron and adjacent carbon atoms give rise to the enhanced toughness. More detailed understanding of the mechanism of the toughness enhancement by the boron/nitrogen co-doping will require additional experiments and detailed theoretical modeling. Figure 1 shows that all boron/nitrogen co-doped CVD diamond has slightly higher hardness compared with undoped CVD diamond. The enhanced growth of both (100) and (111) growth sector appears to strengthen the diamond considerably, as predicted by Anthony *et al* [8].

PL, IR and UV–visible absorption spectra all show significant changes with adjustment of nitrogen in the gas chemistry. With increasing nitrogen content in the gas, the more nitrogen is incorporated on (100) nucleation sites, resulting in a darker brown color in the diamond growth. When (111) growth sectors prevail (with less nitrogen in the gas), boron atoms incorporate into the (111) lattice plane and alter the lattice structure. The color grading for these crystals depends on both the boron and nitrogen concentrations. Defects within diamond layers were significantly reduced by the addition of boron (figure 4). The quality of B-SCD-2 and

B-SCD-3 is as high as type IIa natural diamond, demonstrated by the Raman lineshapes and UV–visible spectra. On the basis of the present results, we suggest that the enhanced optical and mechanical properties of the diamond materials described here may find useful applications as optical windows in harsh environments, mechanical testing, abrasive machining, laser optics, and transparent shielding and MEMS devices. The low cost, large area LPHT annealing process may be an alternative to HPHT annealing and could have important industrial applications.

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